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X-ray microanalysis of grain boundary segregation in steels by s.t.e.m.*

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Equilibrium segregation of Groups IV–VI residual elements during heat treatment (*ca.* 773K) of commercial low alloy steels can significantly modify their toughness, impact properties, corrosion and stress corrosion behaviour and creep life. Since these segregations are highly localized (less than about 10 nm) and do not result in microstructural changes, their direct measurement has proved difficult. The most widely used method to date is Auger electron spectroscopy (A.e.s.). This technique is surface specific, requires uncontaminated intergranularly fractured surfaces and is therefore limited by specimen preparation. The development of scanning transmission electron microscopy (s.t.e.m.) with fine electron probes, *ca.* 15 nm in diameter, when coupled with an energy dispersive analyser enables high resolution X-ray microanalysis within thin foils. This allows grain boundary chemical analysis for elements with atomic number not less than 12. The application of this technique has been investigated by examining segregation of residual elements in experimental iron-based alloys and commercial ferritic steels.

Binary iron–3 % nickel (by mass) alloys, containing minor additions of tin or phosphorus (less than 0.1 % by mass) were heat treated to effect grain boundary segregation (723K, 3.6×10^4 s). Microanalysis of the grain boundary regions showed segregation of the residual elements. By assuming segregation to be confined to a grain boundary 'width' of 1 nm its composition was established from that measured within the volume analysed by the incident electron beam. The measured grain boundary compositions of 14 at. % phosphorus and 2.5 at.% tin were in good agreement with A.e.s. analysis. The high spatial resolution of s.t.e.m. analysis (electron probe diameter, 15 nm, × foil thickness, 200 nm, $\approx 3 \times 10^4$ nm^3) with respect to grain boundary area sampled allows correlation of segregation with microstructure.

The distribution of residual elements in $2\frac{1}{4}$Cr1Mo steel specimens crept at 873K for periods up to *ca.* 10^7 s were measured. The final microstructures were upper bainite containing carbides (*ca.* 0.2 μm diameter) on both the prior austenite and interlath boundaries, and within the bainite laths. Microanalysis showed the following: (*a*) no phosphorus segregation to either prior austenite or interlath boundaries; (*b*) increased silicon and decreased chromium and sulphur concentrations at prior austenite grain boundaries; (*c*) significant phosphorus and sulphur concentration within all intergranular carbides. These results indicate that the residual elements are non-uniformly distributed within grain boundaries and grain boundary carbides.

S.t.e.m. X-ray microanalysis provides a powerful and readily usable technique for detecting and measuring grain boundary segregation. The high spatial resolution combined with the facility for simultaneous examination of microstructure and crystallography provides a useful extension to existing microanalytical techniques.

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